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2. Patent application number (The Patent Office will fill in this part) 0407473.8

3. Full name, address and postcode of the or of each applicant (underline all surnames)

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Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

United Kingdom

4. Title of the invention

Energy-curable inta[illegible]

5. Name of your agent (if you have one)
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8. Is a Patents Form 7/77 (Statement of inventorship and of right to grant of a patent) required in support of this request?

Yes

(Answer 'Yes' if:
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9. Accompanying documents: A patent application must include a description of the invention. Not counting duplicates, please enter the number of pages of each item accompanying this form:

Continuation sheets of this form	0
Description	10
Claim(s)	1
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Priority documents	
Translations of priority documents	
Statement of inventorship and right to grant of a patent (Patents Form 7/77)	
Request for preliminary examination and search (Patents Form 9/77)	1
Request for substantive examination (Patents Form 10/77)	
Any other documents (please specify)	

11. I/We request the grant of a patent on the basis of this application.

Signature(s) Marks & Clerk Date: 1 April 2004

12. Name and daytime telephone number of person to contact in the United Kingdom

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ENERGY-CURABLE INTAGLIO PRINTING INKS

The present invention relates to a novel energy-curable intaglio printing ink, which is especially suitable for printing bank notes.

Intaglio printing, which is sometimes known as "copperplate printing", is well known and is used throughout the world for the printing of banknotes. In intaglio printing, ink is applied under pressure to the engraved surface of a cylinder. Thus, not only does the ink fill the engravings of the cylinder, it is also applied to the planar non-image surface of the cylinder; intaglio is the only printing process in which this occurs. It is thus essential, and almost unique to the intaglio process, that ink must be thoroughly wiped from the planar surface of the engraved cylinder before the printing process is carried out. This is commonly effected by a wiping cylinder contrarotating to the engraved cylinder so that the two surfaces which touch are moving in opposite directions. Given the right conditions and, crucially, the right ink, this will remove the surplus ink from the planar surface as well as a small amount of ink from the surface of the ink in the engravings, so that the only ink on the engraved cylinder is in the engravings. The substrate to be printed is then passed between the engraved cylinder and an impression material, which is typically another cylinder, with the application of considerable pressure between the engraved cylinder and the impression material, which is a hard but deformable material. The considerable pressure deforms the impression material, forcing the substrate to be printed into the engravings on the engraved cylinder. This results in the substrate picking up some ink, corresponding to the engravings on the surface of the engraved cylinder. The ink then has to be dried. Conventionally, this has been done either by the application of heat or, more commonly, by oxidative drying, which has the substantial disadvantage that it may take more than 48 hours to dry fully. However, in recent years, energy curing, e.g. by ultraviolet or electron beam, has become more common in other printing processes and there is a

demand for a similar energy curing process for intaglio printing, since drying is almost immediate.

Because of the unique characteristics of intaglio printing, the inks used for other forms of printing, for example lithographic printing, cannot be used for intaglio, and the formulations tend to be completely different. For example, GB1466470 discloses an ultraviolet-curable ink for copperplate intaglio printing which comprises specific amounts of a curable binder which is an ester or amide of acrylic acid, a pigment, a photoinitiator, an activator for the photoinitiator and an inert extender permeable to ultraviolet light.

GB1469717 discloses an ultraviolet-curable intaglio printing ink comprising a non-ultraviolet setting adduct of tung oil with an unsaturated carboxylic acid and an ultraviolet setting adduct of tung oil with an unsaturated carboxylic acid.

EP432093B1 discloses an ultraviolet-curable intaglio printing ink comprising specific amounts of a pigment, an energy sensitive cationic polymerisation initiator, a viscous binder composition, a compound capable of being polymerised by cationic polymerisation, and a thermoplastic polymeric material which is not cationically polymerisable.

Whilst these prior art documents do disclose inks that may be used for intaglio printing and which are capable of drying by energy curing, they fail to address one crucial matter, namely the ability of the ink to be removed easily from the planar surfaces of the engraved cylinder before printing, without removing the ink within the engravings.

Two methods are currently commonly used to remove surplus ink from the engraved cylinder – paperwipe and waterwipe. In the paperwipe method, crepe paper is applied by means of an oscillating wiper bar under pressure to the surface of the engraved cylinder. The combination of the oscillation of the wiper bar and the rotational movement of the engraved cylinder results in high shear forces being applied to the ink, with the result that surplus ink is adsorbed on the surface and into the folds of the crepe paper and thus effectively removed from the engraved cylinder.

The waterwipe method, sometimes referred to as "cylinderwipe", uses a cylinder coated with a material to which the ink adheres easily, for example polyvinyl chloride (PVC) to remove the surplus ink from the engraved cylinder. The ink has then to be completely removed from the coated surface of the PVC cylinder before that part of the surface returns to contact with the engraved cylinder. This is achieved by a combination of scraping, brushing and washing in an aqueous alkaline bath.

Plainly, the rheology of the ink is critical to its success. In achieving a satisfactory rheology, heat-set inks have an advantage over energy-cured inks, since they can be diluted to achieve a desired viscosity using an organic solvent, which is then removed during the heat-setting process. Energy-curable intaglio inks do not have this advantage and, as a result, tend to be tackier than heat-set inks.

In addition to the rheology and ease of removal of surplus ink, discussed above, intaglio printing inks must meet the following requirements:

They must remain on the engraved cylinder until the moment of printing when they must transfer readily and in a consistent manner to the substrate to be printed.

They must have good film-forming properties and the cured inks must be sufficiently flexible that they remain intact even when the printed matter (e.g. banknotes) are subject to abuse.

Once the substrate has been printed, the ink must not transfer back to other surfaces with which it may come into contact, especially other printed matter.

The cured ink must have excellent chemical and mechanical resistance so as to withstand the many diverse materials and conditions to which banknotes may be subject.

They must be safe for handling by all members of the public, including the very young.

It is also self-evident that, where the ink is to be cured by energy, e.g. ultraviolet or electron beam, any components added to the ink to achieve any of the above

requirements must not interfere with the cure. Not surprisingly, it is difficult to meet all of these desiderata simultaneously.

We have now surprisingly discovered that the incorporation into a conventional ultraviolet-curable intaglio printing ink of any of the well known class of plasticisers will improve the wiping ability of the ink, in both the waterwipe and the paperwipe methods, without any adverse impact on any of the requirements mentioned above.

Thus, the present invention consists in an energy-curable intaglio printing ink comprising a pigment, an energy-curable binder composition, a photoinitiator and a plasticiser.

The term "plasticiser" is used in the printing industry to mean a material which is capable of solvating a film-forming polymer, and materials which serve as plasticisers are well known in the industry. Although the primary function of the plasticiser in the inks of the present invention is not to solvate, and hence plasticise, a polymer, it is possible that they do serve this function in the cured ink, thus enhancing its desirable properties. Instead, we have surprisingly found that the inclusion of the plasticiser enhances the wiping ability of the ink, which is a property of the ink which manifests before the ink is cured.

The plasticiser used should be non-carcinogenic and should be generally recognised as safe to be handled by humans. Preferably, it is a food grade compound.

Examples of suitable plasticisers include:

Abietates, for example: hydroabietyl abietate, hydrogenated methyl abietate, methyl abietate;

Acetates, for example: glyceryl diacetate, glyceryl triacetate, and triethylene glycol diacetate;

Adipates, for example: adipic acid 1,2-propanediol polyester, adipic acid 1,3-butylene glycol polyester, adipic acid benzyl octyl ester, adipic acid benzyl-2-ethylhexyl ester, adipic acid butanediol polyester, di-2-ethylhexyl adipate, dibutyl adipate, diethyl adipate, diisobutyl adipate, diisodecyl adipate, diisononyl adipate,

dimethyl adipate, di-n-C7-C9 adipate, dioctyl adipate, adipic acid n-octyl n-decyl ester, adipic acid polyethylene glycol ester and adipic acid polypropylene glycol ester;

Azelates, for example: di-2-ethylhexyl azelate, dihexyl azelate and dioctyl azelate;

Benzoates, for example: butyl benzoate, benzoic acid diethylene glycol ester, benzoic acid dipropylene glycol ester, glyceryl tribenzoate, neopentylglycol dibenzoate, polyethylene glycol 200 dibenzoate, polyethylene glycol 400 dibenzoate, pentaerythritol tetrabenzoate, 2-ethylhexyl p-oxybenzoate, benzoic acid sucrose ester, and triethylene glycol dibenzoate;

Butyrates, for example: glyceryl tributyrate, 2,2,4-trimethyl-1,3-pentanediol diisobutyrate, and 2,2,4-trimethyl-1,3-pentanediol mono(2-methylpropionate);

Caprylates, for example: di(triethylene glycol dioctanoate) caprylate;

Citrates, for example: acetyl tri(2-ethylhexyl) citrate, acetyl tributyl citrate, acetyl triethyl citrate, tributyl citrate, tricyclohexyl citrate, triethyl citrate, and triisoamyl citrate;

Epoxidised, for example: 2-ethylhexyl esters of epoxidised tall oil, epoxidised linseed oil, epoxidised soya fatty acid ethylhexyl ester, epoxidised soybean oil,

Fumarates, for example dibutyl fumarate;

Glutarates, for example dimethyl glutarate;

Hexanoates, for example: polyethylene glycol 200 di-2-ethylhexyl hexanoate, polyethylene glycol 400 di-2-ethylhexanoate, and polyethylene glycol di-(2-ethylhexanoate);

Lactates, for example: ethyl lactate, isopropyl lactate, and n-butyl lactate;

Laurates, for example: polyethylene glycol 200 monolaurate, polyethylene glycol 400 dilaurate, polyethylene glycol 400 monolaurate, and polyoxyethylene laurate;

Maleates, for example: dibutyl maleate, diisobutyl maleate, diisooctyl maleate, and dioctyl maleate;

Oleates, for example: diglyceryl oleate, epoxidised octyl oleate, monoglyceryl oleate, n-butyl oleate, n-heptyl oleate, oleic acid polyethylene glycol 200, 400 and 600 esters, oleic acid polyethylene glycol diester, oleic acid polyethylene glycol monoester, oleic acid sorbitol ester, tetrahydrofurfuryl ester, oleic acid tetra-sorbitol ester, oleic acid tri-glycerol ester, and oleic acid tri-sorbitol ester;

Palmitates, for example: cetyl palmitate and palmitic acid polyethylene glycol monoester;

Phosphates, such as diphenyl 2-ethylhexyl phosphate, diphenyl isodecyl phosphate, diphenyl octyl phosphate, tri(2-ethylhexyl) phosphate, tributoxyethyl phosphate, tributyl phosphate, triethyl phosphate, trioctyl phosphate, and triphenyl phosphate;

Phthalates, for example: butyl phthalyl butyl glycolate, ethyl phthalyl ethyl glycolate, benzyl phthalate, benzyl butyl phthalate, benzyl octyl phthalate, butyl phthalate, methyl phthalate, carboxybutyl phthalate, butyl octyl phthalate, 2-ethylhexyl phthalate, dicyclohexyl phthalate, didecyl phthalate, diethyl phthalate, diheptyl phthalate, diheptyl nonyl phthalate, dihexyl phthalate, diisobutyl phthalate, diisodecyl phthalate, diisoheptyl phthalate, diisononyl phthalate, diisooctyl phthalate, diisotridecyl phthalate, dimethoxyethyl phthalate, dimethyl phthalate, dimethylcyclohexyl phthalate, phthalic acid C6-C10 ester, phthalic acid C7-C11 ester, phthalic acid C8-C10 ester, phthalic acid C8-C12 ester, phthalic acid C9-C11 ester, dibutyl phthalate, phthalic acid C10-C12 ester, dioctyl phthalate, diphenyl phthalate, di-tridecyl phthalate, di-undecyl phthalate, heptyl phthalate, nonyl phthalate, undecyl phthalate, hexyl phthalate, octyl phthalate, and decyl phthalate;

Polyol esters, for example polyethylene glycol 400, polypropylene glycol hexamethylene diisocyanate copolymer, polypropylene glycol, and polypropylene glycol tolylene diisocyanate copolymer;

Ricinoleates, for example butyl acetyl ricinoleate, butyl ricinoleate, ethylene glycol ricinoleate, glyceryl monoricinoleate, glyceryl tri(acetyl ricinoleate), glyceryl triricinoleate, methyl acetyl ricinoleate, methyl ricinoleate, polyethylene glycol monoricinoleate, and propylene glycol monoricinoleate;

Sebacates, for example: sebacic acid 1,2-propanediol polyester, di-2-ethylhexy sebacate, dibutyl sebacate, and dioctyl sebacate;

Stearates, for example: 12-hydroxystearic acid, glyceryl tri(12-hydroxystearate), isobutyl stearate, butyl stearate, stearic acid octyl epoxy ester, and stearic acid polyethylene glycol 400 diester;

Tall oil esters, for example: 2-ethylhexyl tallate, isooctyl tallate, and octyl epoxy tallate;

Other esters, for example: diethylene glycol dipelargonate, diethyl hexanedioic acid, dimethyl hexanedioic acid, linseed oil maleinate, methyl phthalyl ethyl glycolate, polyethylene glycol ester of castor oil, dilauryl thiodipropionate, dimethyl succinate, and sucrose aceto isobutyrate;

Sulphonamides, for example: N-butyl sulphonamide, butyl benzyl sulphonamide, cyclohexyl p-toluenesulphonamide, toluenesulphonamide-formaldehyde condensation product, o-ethyl-p-toluenesulphonamide, N-butyl-p-toluenesulphonamide, N-cyclohexyl-p-toluenesulphonamide, N-ethyl-o-toluenesulphonamide, N-ethyl-o,p-toluenedisulphonamide, N-ethyl-p-toluenesulphonamide, o-toluenesulphonamide, o,p-toluenedisulphonamide, and p-toluenesulphonamide;

Others, for example: butylurethane-formaldehyde copolymer, butyl carbamate, hydrogenated castor oil, di(phenoxyethyl) formal, diethyldiphenylurea, ethoxylated glycerol, ethoxylated fatty alcohol, formaldehyde-urea copolymer, ethoxylated glycerol, and polyethylene glycol monobutyl ether.

Of these, we particularly prefer the sebacates, citrates and toluenesulphonamides.

We particularly prefer that the plasticiser should have a molecular weight of from 100 to 500, more preferably from 150 to 350.

We also particularly prefer that the plasticiser should have a boiling point at STP of from 100 to 500°C, more preferably from 150 to 350°C.

The remainder of the components of the energy-curable intaglio printing inks of the present invention are well known for use in this type of ink and may be found in the prior art, for example that mentioned above.

The curing conditions are likewise well known in the art and are essentially the same as those for the known inks referred to above.

The invention is further illustrated by the following non-limiting Examples.

EXAMPLES 1 & 2

The ingredients of the ink, as shown below in Table 1 for a waterwipe ink (Example 1) and Table 2 for a paperwipe ink (Example 2), were weighed and mixed to form a paste. The paste was then fully mixed and dispersed using a three roll mill to produce a homogeneous, viscous paste ink.

Table 1

Material	Amount (wt %)	Supplier
Ebecryl 657 (polyester acrylate)	30	UCB chemicals
SMA1440F (acidic acrylate resin)	10	Cray Valley
Sartomer 494 (ethoxylated pentaerythritol tetraacrylate)	17	Cray Valley
Chromophtal LGLD (blue pigment)	5	CIBA
Irgacure 819 (photoinitiator)	4.9	CIBA
Talc D2002	20.1	Omya
Carnauba Wax	3	Eggar
Empilan CDE (Coconut diethanolamide – surfactant)	4	Huntsman
Turkey Red Oil (sulphonated castor oil)	2	J&W Whewell
Dibutyl sebacate	3	Edenol DBS Cognis
Florstab UV-1 (UV stabiliser)	1	Kromachem
Total	100	

Table 2

Material	Amount (wt %)	Supplier
Ebecryl 648 (epoxy acrylate)	55	UCB chemicals
Sartomer 494 (ethoxylated pentaerythritol tetraacrylate)	3	Cray Valley
Chromophtal LGLD (blue pigment)	5	CIBA
Microtalc IT extra	23.1	Omya
Corn Starch	2	Cerestar
Carnauba wax	3	Eggar
Dibutyl sebacate	3	Edenol DBS Cognis
Irgacure 819 (photoinitiator)	4.9	CIBA
Florstab UV-1 (UV stabiliser)	1	Kromachem
Total	100	

A UV ink was applied to an intaglio plate, and wiped by hand using crepe paper. A print was taken from the wiped plate and the amount of ink left in the planar non-image area was assessed visually. The addition of a plasticiser provided a clean print in that there was no ink in the planar non-image and was a considerable improvement over UV intaglio inks without the addition of plasticiser.

CLAIMS:

1. An energy-curable intaglio printing ink comprising a pigment, an energy-curable binder composition, a photoinitiator and a plasticiser.

2. A printing ink according to Claim 1, wherein the plasticiser is food grade.

3. A printing ink according to Claim 1 or Claim 2, wherein the plasticiser has a molecular weight of from 100 to 500.

4. A printing ink according to Claim 3, wherein said molecular weight is from 150 to 350.

5. A printing ink according to any one of Claims 1 to 4, wherein the plasticiser has a boiling point of from 100 to 500°C.

6. A printing ink according to Claim 5, wherein the boiling point is from 150 to 350°C.

7. A printing ink according to any one of Claims 1 to 6, wherein the plasticiser is a sebacate.

8. A printing ink according to Claim 7, wherein the sebacate is dibutyl sebacate.

9. A printing ink according to any one of Claims 1 to 6, wherein the plasticiser is a citrate.

ABSTRACT:

The wiping ability of an energy-curable intaglio printing ink is improved by the incorporation therein of a plasticiser.

REGISTER ENTRY FOR GB0407473.8

Form 1 Application No GB0407473.8 filing date 01.04.2004

Title ENERGY-CURABLE INTAGLIO PRINTING INKS

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